PATENT SPECIFICATION

660,017

Date of Application and filing Complete Specification: Oct. 6, 1948.

No. 26035/48.

Application made in Netherlands on Oct. 11, 1947.

Complete Specification Published: Oct. 31, 1951.

Index at acceptance:—Classes 1(i), F6; 2(iii), C3a(7 : 10e4), V; and 91, B2a, C2a1.

COMPLETE SPECIFICATION

Improvements in or relating to the Separation of Fatty Acids and Fatty Acid Derivatives

We, LEVER BROTHERS & UNILEVER LIMITED, a Company registered under the Laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

In U.S. patent specification 2,408,625 it has been proposed to dialyse the fat-solvent extracts of grass, alfalfa, spinach, root-crops and other vegetable material through a rubber membrane. Vitamins and pro-vitamins in addition to sterols dialyse through the rubber membrane while chlorophyll and other substances soluble in fat-solvents are retained. The dialysis is applied in order to separate carotene, vitamin K and xanthophyll from the bulk of the chlorophyll.

In British patent specification No. 592,587 there is disclosed a process for the dialysis of solutions comprising passing the solution to be dialysed through the annulus between a tubular dialyser of relatively large diameter and a tubular dialyser of smaller diameter which is disposed inside the larger tubular dialyser. Another liquid is passed through and in contact with the tubular dialyser of smaller diameter and a third fluid is passed over the external surface of the larger tubular dialyser. The specification also discloses that when it is desired to separate a hydrophobic organic liquid from water or organic compounds of a different type there may be employed tubes formed of hydrophobic colloidal materials as a class of which there may be given by way of example, tubes formed of synthetic resins such as polyvinyl resins, methyl methacrylate resins, chloroprene, nylon and chlorinated rubber or from an organic solvent-soluble cellulose derivative. The specification further discloses that when hydrophobic tubes are employed they are preferably used in the swollen gel state, that is, while they are saturated with the organic liquid which it is desired to evaporate through the tube.

It has now been found that components of fatty oils or of derivatives thereof containing oily constituents can be separated or extracted by dialysis through a membrane of a high polymeric substance, such as rubber, which exhibits swelling with the substance to be dialysed or with a solvent used in the dialysis. It has been found that fatty acids with at least 4 carbon atoms or their derivatives diffuse through a rubber membrane at varying velocities and in such a way that a separation of the fatty acids or their derivatives containing oily constituents from each other or an extraction of these substances from mixtures containing other substances can be achieved; inter alia, fatty acids, triglycerides as found in normal oils and fats, and esterified vitamin A can be easily dialysed, but polymerised glycerides, mono- and diglycerides, metallic soaps, phosphatides, mucilage and the coloured substances which give oils and fats an unwanted, often reddish colour, for example, are less easy to dialyse. The substances which will dialyse easily show variations in the velocity of dialysis so that they can also be separated one from another. Hence it is possible to clarify fatty acids or fatty acid derivatives containing oily constituents, particularly oils and fats or their residual products, by dialysis through a rubber membrane, thus removing the badly coloured and/or other unwanted substances. It is also possible to concentrate certain constituents of mixtures of fatty acids or fatty acid derivatives containing oily constituents. Further details of this for a number of cases will be given in the examples.

According to the present invention, in the separation or extraction of the components of fatty oils or of their derivatives containing oily constituents, there is applied dialysis by means of a membrane of a high polymeric substance which exhibits swelling with the

[*Price 2/8*]

substance to be dialysed or with a solvent used in the dialysis. Further according to the present invention there is provided a method for separating or extracting components of fatty oils or of products derived therefrom wherein said oils or products, with or without admixture of a solvent, are dialysed through a membrane consisting of a high polymeric substance which exhibits swelling with the substance to be dialysed or with the solvent used in the dialysis.

Rubber and rubber-like substances in the widest sense may be used for the membrane; thus the rubber may be vulcanised or not and both natural and synthetic rubber can be used. A suitable rubber-like substance is, for example, gutta percha.

Instead of rubber or rubber-like substances, however, other high-polymeric substances which exhibit swelling with the substances to be dialysed or with the solvents may be used, for example a methyl or ethyl polyacrylic acid ester, polyvinyl chloride copolymerised with a small amount of polyvinylidene chloride (the plastic known under the Registered Trade Name "Geon"), and polyvinyl chloride.

Preferably a solution of the substances to be separated or extracted in a volatile solvent or mixture of solvents is subjected to dialysis. It is advantageous to take a concentrated solution and to put the solvent or a dilute solution of the fatty substances on the other side of the membrane. There may also be used two or more solvents which show only a limited intermiscibility and which, preferably before dialysis, are saturated with each other; one liquid is introduced on the one side, the other on the other side of the membrane.

The polarity of the solvent and of the substances to be separated is important. In order to retard dialysis of polar substances through the membrane, a strongly polar solvent may be used or a more strongly polar solvent may be added to an existing solvent. Conversely dialysis of polar substances can be accelerated by using a less polar solvent or mixture of such solvents.

The course of the dialysis is likewise dependent upon the material used for the membrane. Thus by a correct choice of the kind of rubber (for example natural or synthetic rubber, non-vulcanised or more or less highly vulcanised rubber and the like), it is possible to influence separation. The polarity of the rubber is particularly important. The term polar is given to rubber when it comprises polar groups, for example, the nitrile-group; perbunan is an example of this, while polyisobutylene is a non-polar rubber. By applying a more highly polar kind of rubber it is possible to accelerate dialysis of polar substances and on the other hand, by applying a less polar rubber, to retard it.

It is often desirable to carry out fractional dialysis. It is possible, for example, to redialyse the dialysate (that is that portion which has already once passed through the membrane) against fresh solvent or against a less concentrated solution and, if desired, to repeat this process several times. The residues (that is the parts retained by the membrane) obtained consecutively can again be added to the starting material, if desired after removal of solvent.

In order to prevent damage to the rubber membrane, it is often advisable to provide it with mechanical protecting means, for instance by supporting it with metal gauze. It may also be useful to dissolve a substance, preferably non-diffusing, in the liquid, on the dialysate side in such a concentration that it makes the liquids on both sides of the membrane at least isotonic.

Dialysis may be continuous as well as discontinuous. In the former case it is preferable to operate on the counter-current principle.

Dialysis may be carried out at room temperature or at an elevated temperature. An elevated temperature has, in general, the advantage that the velocity of dialysis is greater.

In the following examples dialysis was carried out on a small scale by filling a rubber sleeve made of Heavea rubber containing 2% sulphur, a little zinc oxide and an ultra-accelerator, which has been vulcanised for one hour at 80° C, and with a wall thickness of several tenths of a mm., with a solution of the substances to be separated or extracted and placing it in the pure solvent which was renewed several times. On a practical scale the usual methods can be applied for promoting separations, for limiting the quantity of solvent and for accelerating dialysis, such as raising the temperature, applying counter-current, fractional dialysis and the like.

EXAMPLE 1.

Demucilaging of crude groundnut oil.

A 1 : 1 solution of crude groundnut oil in petroleum ether contained in a rubber sleeve of 0.40 mm. wall-thickness was suspended in 1.5 litres of petroleum ether which was renewed now and again until there was practically no further dialysis. The dialysate was obtained by distilling the petroleum ether from the resulting solutions. In total 97.8% of the oil was recovered in the dialysate. Whereas the original groundnut oil frothed very strongly when shaken, the dialysate did not froth at all. At the same time the colour was greatly improved: the Lovibond colour (2" cell) of the original crude

oil was 45 yellow + 4.5 red, while for the demucilaged oil it was 16 yellow + 1.0 red. The residue, which still contained oil, amounted to 2.3%; it was dark brown and treacly and frothed very strongly.

This clarification is important for the refining of edible oils, because the removal of the impurities in the manner described above makes possible a considerable simplification of the subsequent refining. As an example it may be mentioned that the dialysate obtained according to this example, which contained 7.1% free fatty acid gave, after steam distillation at 225° C, a good salad oil with 0.28% free fatty acid; colour (2" Lovibond): 9 yellow + 1.45 red. On the other hand, the original oil discoloured on such distillation to 90 yellow + 21 red.

EXAMPLE 2.

Separation of phosphatides and oil.

A 1 : 1 solution of 10 g. of soya phosphatides with a phosphatide content of 59.4% (calculated from the phosphorus content) in petroleum ether was suspended in a rubber sleeve in petroleum ether. After 24 hours and after the petroleum ether had been renewed several times, 32% appeared to have dialysed through the sleeve. The dialysate consisted of light-coloured oil and fatty acids and was free from nitrogen and phosphorus. According to the phosphorus content the residue comprised 87.1% phosphatides.

In this way it is possible, if found desirable, to remove the fatty portion of crude oils with a high free fatty acid content from soya phosphatides and to replace it by another oil or fat.

A corresponding test with rapeseed oil phosphatides was continued for three days, the petroleum ether being renewed twelve times in total. Here too, the dialysate was free from nitrogen and phosphorus. The solid residue could be powdered; it dissolved in the mouth and tasted like yeast and, compared with the starting material, the taste was greatly improved.

EXAMPLE 3.

Extraction of vitamin A fatty acid ester from fish liver oils.

10 g. of an oil which contained vitamin A ester in a concentration of 15,000 international units per gram, was dissolved in 40 cc. of petroleum ether, and was dialysed in a rubber sleeve against 450 cc. of petroleum ether. After 1½ hours the quantity of dialysate (after renewing the solvent) was 16.8% with a content of 27,500 international units per gram of vitamin A ester.

The same test was repeated with acetone as solvent when, after 16 hours, 26.4% dialysate with 27,500 international units per gram of vitamin A ester was obtained.

Separation by dialysis

	n_D^{65}	Percentage
Original stand oil	1.4725	—
Residue	1.4765	62.5%
Dialysate .. .. (or oil dissolved in acetone).	1.4621	37.5%

The refractive indices show (although they are not additive with this kind of oil) that separation by dialysis is more effective.

EXAMPLE 4.

Extraction of polymers.

20 g. of a dehydrated castor oil was dissolved in 40 cc. of petroleum ether; the solution was dialysed in a rubber sleeve against 500 cc. of petroleum ether. After 18 hours, 48.7% of the oil had passed through the rubber membrane. This part consisted of light-coloured, thin oil. The residue was dark-coloured and very viscous. The change in properties appears from the following table:—

	n_D^{65}	diene number
Original oil ..	1.4677	30.5
Dialysate ..	1.4670	40.5
Residue ..	1.4678	—

By the treatment the oil was refined in the sense that constituents which soften the film are removed. At the same time the colour was greatly improved.

EXAMPLE 5.

Extraction of polymers.

50 g. of stand oil from linseed oil, dissolved in an equal volume of petroleum ether, was dialysed in a rubber sleeve against 800 cc. of petroleum ether which was renewed once. 62.5% residue was obtained which had far better properties than the original oil for use in the paint industry.

The separation obtained was compared with the preparation of "separated stand oil" by partially dissolving the oil in acetone.

Separation by dissolving in acetone

	n_D^{65}	Percentage
	1.4725	—
Not dissolved in acetone	1.4750	54.0%
Dissolved in acetone	1.4696	45.9%

EXAMPLE 6.

Separation of partial glycerides.

5 g. portions of a mixture of mono-, di-

and tri-laurines with 41 to 42% monoglycerides, hydroxyl number 280, and 2.4% free lauric acid dissolved in mixtures of petroleum ether and alcohol were dialysed through rubber sleeves of 0.29 mm. wall-thickness against mixtures of petroleum ether and alcohol, the proportions of petroleum ether to alcohol in the mixtures being respectively 1 : 2, 1 : 1 and 2 : 1 being used. After dialysing for one night, the content of monoglycerides in the dialysate and in the residue was determined.

Ratio petroleum ether : alcohol	1 : 2		1 : 1		2 : 1	
	quantity	content	quantity	content	quantity	content
Dialysate	24.3%	10.6%	20.1%	17.5%	50.3%	33.4%
Residue	75.7%	52.0%	49.9%	48.0%	49.7%	50.3%

It is striking that all three residues contain approximately the same content of monoglycerides, although they form greatly varying percentages of the starting material. This is explained by the fact that trilaurine dialyses much more quickly than mono- and dilaurine and monolaurine about as quickly as dilaurine. The extraction of triglycerides from mixtures with mono- and diglycerides is, inter alia, of importance when it is desired to prepare detergents from the last-mentioned substances by sulphating.

It further appears from this example that according to the extent to which the solvent contains more alcohol which is a strongly polar liquid, the dialysis of the strongly polar monoglycerides is retarded. Further this example shows that the velocity of dialysis is governed, not only by the size of the molecules but also by the polarity of the dialysing substances.

EXAMPLE 7.

Purification of extraction fat from nickel catalyst.

In the extraction with benzine of nickel catalyst used for hardening of fat, a fat is often obtained which is coloured deep black by colloidally dissolved nickel that is difficult to remove. The solution of such an extraction fat in petroleum ether runs through filter paper without leaving any residue behind. If the solution is dialysed in a rubber sleeve against petroleum ether, however, then the dialysate is light yellow and free from nickel. In the case of a particularly poor sample of extraction fat only 60% appeared to be dialysable and the residue consisted of a black solid substance.

EXAMPLE 8.

Purifying poor herring oil.

A particularly poor, dark herring oil with about 50% free fatty acid and a high content of oxy-acids was dissolved in an equal quantity of petroleum ether and dialysed in a rubber sleeve against petroleum ether. In total 81% of the starting material dialysed. This dialysate was coloured light yellow, while the residue consisted of hard crusts. The latter could be avoided by not carrying on dialysis so far.

EXAMPLE 9.

Purifying refinery acid oils.

The acid oils obtained during the neutralising of crude oils by splitting refinery soap are usually of such poor quality that without special purification they cannot be made into good soap. Dialysis of such acid oils gave the following results :—

(a) Acid oils from fish oil, whose Lovibond colour in the $\frac{1}{4}''$ cell was 120 yellow + 80 red, were dialysed in a 1 : 1 solution in petroleum ether through a rubber sleeve of 0.3 mm. wall thickness against petroleum ether. 96.3% dialysate was obtained with a colour ($\frac{1}{4}''$ cell) 15 yellow + 13 red, so that a very great improvement in colour was achieved.

(b) Acid oils from coconut oil, whose colour ($\frac{1}{4}''$ cell) was 60 yellow + 10.2 red, gave 99.2% dialysate with colour ($\frac{1}{4}''$ cell) 7 yellow + 1.6 red.

By treating the dialysate with bleaching earth a further improvement in colour was achieved.

HAVING NOW particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is :—

1. A method for separating from fatty oils or their derivatives containing oily constituents substances contained therein, wherein said oils or derivatives, with or without admixture of a solvent, are dialysed by means of a membrane consisting of a high polymeric substance which exhibits swelling with fatty oils.

2. A method as claimed in Claim 1 wherein said high polymeric substance is rubber.

3. A method as claimed in Claim 2 wherein said rubber is vulcanised.

4. A method as claimed in Claim 1 wherein said high polymeric substance is a methyl or ethyl poly-acrylic acid ester, or polyvinyl chloride.

5. A method as claimed in Claim 1 wherein said high polymeric substance is polyvinyl chloride copolymerised with a small amount of polyvinylidene chloride.

6. A method as claimed in any of the preceding claims when applied to the extraction or concentration of vitamin A fatty acid ester.

7. A method as claimed in any of the Claims 1–5 when applied to the separation of partial glycerides.

8. A method as claimed in any of the Claims 1–5 when applied to the treatment of polymerised oils.

9. The methods of separating components of fatty oils and their derivatives containing oily constituents substantially as herein described.

10. Components of fatty oils and their derivatives containing oily constituents when separated by the methods as claimed in any of the preceding claims.

Dated this 6th day of October, 1948.

LEVER BROTHERS & UNILEVER LIMITED.

R. JONAS,

Acting for the Applicants.

PUBLISHED BY:-
THE PATENT OFFICE,
25, SOUTHAMPTON BUILDINGS,
LONDON, W.C.2.